

Ultra-high strength polyethylene filaments by solution spinning/drawing. 3. Influence of drawing temperature

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(Received 24 April 1980)

The influence of the temperature on the drawing behaviour of gel-fibres, which were obtained by spinning of a 2% w/w solution of high molecular weight polyethylene ($\bar{M}_w = 1.1 \times 10^6$) in decalin, was studied in the range from 70 to 143°C. It was found that the drawing temperature, like the presence of solvent in the gel-fibres, affected the maximum attainable draw ratio, but did not influence the effectiveness of the hot drawing below the melting point of the polymer.

INTRODUCTION

The drawing behaviour at elevated temperatures of melt-crystallized linear polyethylene has been the subject of many investigations¹⁻⁷. The primary objective of the more recent studies, notably by Capaccio and Ward, was to produce ultrahigh-modulus polyethylene structures⁴⁻⁷. It was found that the temperature range over which linear polyethylene can be effectively drawn to high draw ratios, depends on the molecular weight and its distribution. For each polyethylene sample there appear to be optimal conditions for producing highly oriented structures by drawing. These cited studies were mainly focussed on polyethylenes with molecular weights (\bar{M}_w) lower than 300 000. High molecular weight polyethylene, which is of particular interest for improved creep properties and potential high strength, could not be effectively drawn to such an extent that very high moduli were obtained⁵. In order to achieve high draw ratios for these materials the drawing temperature had to be raised to such high values, in fact above the melting temperature of the polymer, that drawing occurred with a highly reduced effectiveness⁵.

Recently, we reported a drastically enhanced effective drawability of high molecular weight polyethylene that was spun^{8,9} or cast¹⁰ from semi-dilute solutions to form macroscopic gels. It was found that polyethylene gel-fibres, which were produced by spinning of a 2% w/w solution of high molecular weight polyethylene ($\bar{M}_w = 1.5 \times 10^6$) in decalin, could readily be drawn to a draw ratio of 30 at a temperature of 120°C and a strain rate of 1 s⁻¹. Melt-crystallized fibres of the identical polymer sample could not be elongated by more than 5 times under the same drawing conditions⁹. The excellent mechanical properties of the highly drawn solution spun filaments are reflected by a room temperature Young's modulus of 90 GPa and a tensile strength of 3 GPa. The role of the solvent, that initially was present in the polyethylene gel-fibres, in the deformation process was discussed previously^{9,10}. It was established that the diluent had some plasticizing effect⁹, but the main cause for the greatly increased effective drawability of high molecular weight poly-

ethylene was shown to be the strongly reduced number of entanglements in the polymeric structures generated from semi-dilute solutions, in comparison with melt-crystallized material^{9,10}.

In our previous studies drawing of the solution spun gel-fibres was invariably performed at a temperature of 120°C. The present communication deals with the effect of the temperature on the drawing behaviour of both wet and fully dried gel-fibres. The results of this study may be complementary to those obtained by other authors in drawing melt-crystallized material of lower molecular weight, and may provide additional understanding of the mechanism of drawing partially disentangled high molecular weight polyethylene.

EXPERIMENTAL

A linear polyethylene with $\bar{M}_w = 1.1 \times 10^6$ and $\bar{M}_n = 1.5 \times 10^5$ was used in this study. The solvent was decalin from J. T. Baker Chemicals. The methods of spinning, hot drawing and sample preparation and characterization were identical to those described previously^{8,9}. Polyethylene fibres were spun from a 2% w/w solution at 130°C. The as-spun liquid threads were quenched in cold water to form continuous gel-fibres, which contained almost 98% w/w of decalin. One set of gel-fibres was drawn immediately after they were generated. A second group of these gel-filaments was dried at room temperature at constant length, and they were subsequently extracted with ethanol to remove the last trace of solvent. These solvent-free fibres were also drawn to various draw ratios at temperatures ranging from 70-143°C. The strain rate employed was ~ 1 s⁻¹. The draw ratios quoted in this paper refer to the reduction in cross-sectional area (calculated from the mass per unit length) of the drawn filaments relative to the undrawn dried fibres.

The mechanical properties of the drawn filaments were tested at room temperature employing an Instron tensile-tester. The initial sample length was 15 cm and the testing speed was 5 cm min⁻¹. The Young's moduli presented hereafter indicate the initial moduli.

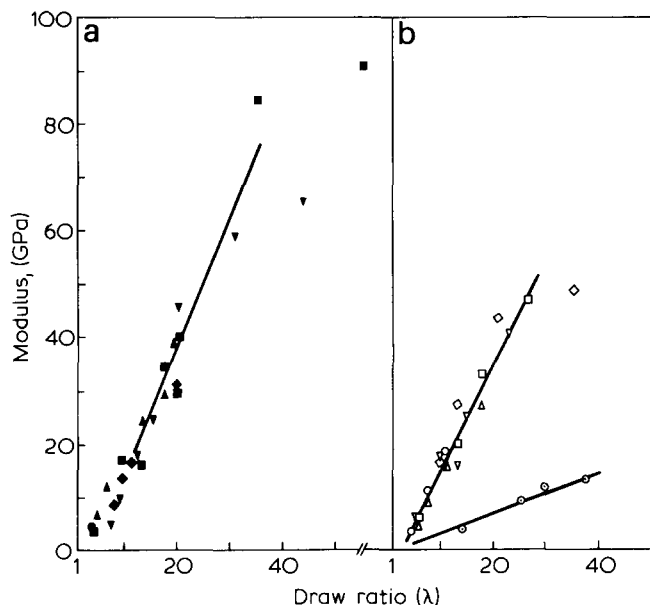


Figure 1 Young's modulus/draw ratio relationship for polyethylene. (a) Initially wet gel-fibres; drawing temperatures: ●, 70°C; ▲, 93°C; ■, 106°C; △, 120°C; ◆, 133°C. (b) Fully dried gel-fibres; drawing temperatures: ○, 70°C; △, 93°C; □, 106°C; △, 120°C; ◇, 133°C; ○, 143°C

RESULTS AND DISCUSSION

Modulus

The Young's modulus is plotted against the draw ratio for the initially wet and fully dried gel-fibres, resp. in Figures 1a and b, drawn at various temperatures. In both cases we observed a linear relationship between the modulus and the draw ratio (λ) for $\lambda < \sim 30$. This linear relation was reported previously by a number of authors for drawing of melt-crystallized polyethylene⁴⁻⁷ and in part 1 of this series⁸. At values of λ exceeding 30 the Young's modulus tended to depart from the straight curve. Jarecki and Meier⁷ observed a similar behaviour in drawing lower molecular weight polyethylene crystallized from the melt and these authors attributed the deviation from linearity to an internal voiding process.

It is seen in Figure 1 that in the linear region the drawing temperature virtually had no influence on the effectiveness of the drawing process (i.e. the slope of the modulus/ λ -curve) in the range from 70–133°C. At a temperature of 143°C, which is above the melting point of the pure polymer, drawing became much less effective due to partial relaxation of the macromolecules, or, in the case of the wet gel-fibres, impossible.

The most striking feature of Figure 1 is that the effectiveness of the hot-drawing was not affected by the initial presence or absence of the solvent in the gel-fibres. This can be inferred from the fact that the slopes of the modulus/ λ -curves in Figures 1a and b are identical. This finding was described earlier in a preliminary account of this work⁹. The effect of drying of the gel-fibres on their drawing behaviour was reflected in the maximum draw ratio achieved (see below).

Tensile strength

In Figures 2a and b the tensile strengths of the various drawn polyethylene filaments are presented. Once more we observed that the initial presence of solvent in the gel-

fibres and the drawing temperature ($< 143^\circ\text{C}$) had no effect on the final strength of fibres with a given draw ratio. As noted previously⁸, the tensile strength appeared to approach an upper limit at high draw ratios. This maximum value is determined by the molecular weight of the polymer used. The current maximum tensile strength for the present polyethylene sample, having a molecular weight (\bar{M}_w) of 1.1×10^6 , was 2.8 GPa of a filament with a Young's modulus of 91 GPa. This value is slightly lower than the strength of 3.0 GPa obtained previously^{8,9} for a highly oriented filament of polyethylene with $\bar{M}_w = 1.5 \times 10^6$, which had the same Young's modulus. On the influence of the molecular weight on the tensile strength of these ultrahigh-modulus polyethylene fibres will be reported in part IV of this series.

Maximum draw ratio

The draw ratios achieved in drawing fully dried and initially wet gel-fibres at various temperatures are presented in Figure 3 (respectively curves a and b). The maximum draw ratio for the dried gel-fibres increased

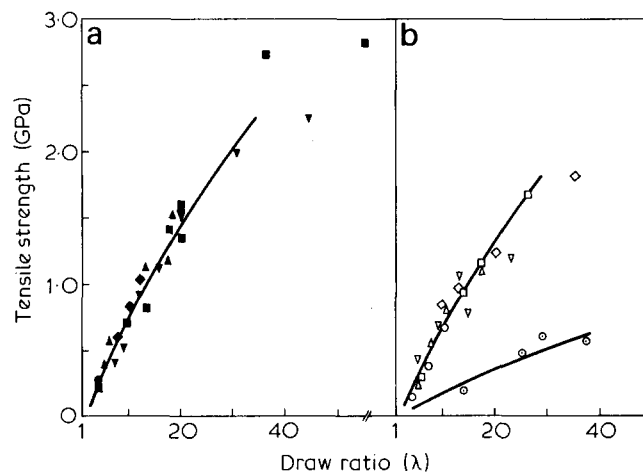


Figure 2 Tensile strength/draw ratio relationship for initially wet (a) and dried (b) polyethylene gel-fibres. Legend see Figure 1

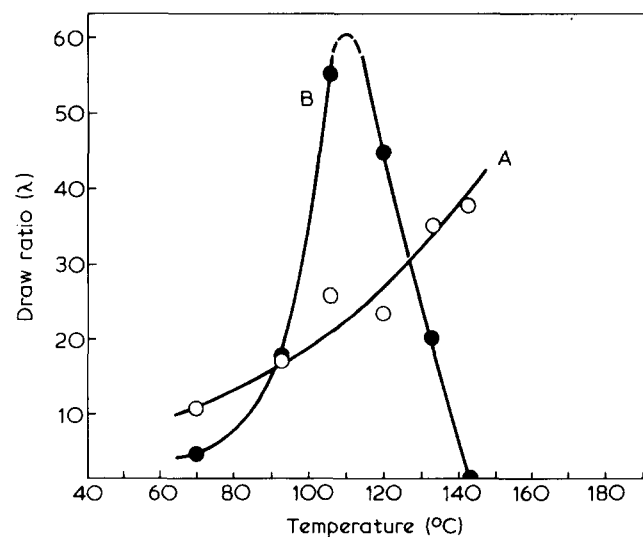


Figure 3 Maximum draw ratio versus drawing temperature for dried (a) and wet (b) gel-fibres of high molecular weight polyethylene ($\bar{M}_w = 1.1 \times 10^6$)

continuously with increasing drawing temperature (curve a), which is quite similar with observations by Capaccio and Ward for melt-crystallized polyethylene with $\bar{M}_w = 312\,000^5$. In drawing the wet gel-fibres, by contrast, there appeared to be a maximum in the λ /drawing temperature curve around 110°C (curve b). In the temperature range from 90–125°C the maximum draw ratio achieved for the initially wet gel-fibres was substantially higher than for the gels that were dried prior to drawing. Here the solvent had a plasticizing effect in the drawing process, similar with low molecular weight material present in melt-crystallized polyethylene⁶.

It is interesting to note that the lower bound temperature of the optimal region for drawing wet gel-fibres (90°C) agrees very well with the 'dissolution' temperature of the polyethylene gels⁸. The upper bound temperature of 125°C, on the other hand, is in accord with the dissolution temperature of oriented polyethylene filaments under strain¹¹. At temperatures >120°C the maximum draw ratio attainable for wet gel-fibres rapidly dropped to low values. This is likely to be due to the lack of strength of the polyethylene gels, which were completely dissolved at these high temperatures.

The optimal temperature range for drawing wet gel-fibres virtually coincides with the region where the so-called 'surface growth' technique of Zwijnenburg and Pennings¹² has been performed successfully. This observation seems once more⁸ to point to a close resemblance between the surface growth process and the present hot drawing of polyethylene gels. This resemblance was also stressed, and illustrated with elegant experiments by Barham *et al.*¹³.

A final remark should be made on the values of the

'maximum' draw ratios presented in this paper. The values depend on the strain rate, particularly for wet gel-fibres. If the hot drawing of these gels is carried out very slowly (much slower than the currently adapted strain rate of $\sim 1\text{ s}^{-1}$), the initially wet gel-fibres dry out before the drawing process is completed. The maximum draw ratio then achieved will no longer be given by curve b in Figure 3. Nevertheless, the following conclusions can be drawn from this study:

- (1) The effectiveness of hot drawing of gels of high molecular weight polyethylene is not influenced by the presence of solvent in the gel-fibres.
- (2) The 'maximum' draw ratio for dried gel-fibres gradually increases with increasing drawing temperature, whereas the maximum draw ratio/drawing temperature curve for wet gels exhibits a maximum.

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